

10528256.trn

Connecting via Winsock to STN

Welcome to STN International! Enter x:x

LOGINID:SSSPTA1626GMS

PASSWORD:

TERMINAL (ENTER 1, 2, 3, OR ?):2

* * * * * Welcome to STN International * * * * *

NEWS 1 Web Page URLs for STN Seminar Schedule - N. America
NEWS 2 JAN 08 CHEMLIST enhanced with New Zealand Inventory of Chemicals
NEWS 3 JAN 16 CA/CAPLUS Company Name Thesaurus enhanced and reloaded
NEWS 4 JAN 16 IPC version 2007.01 thesaurus available on STN
NEWS 5 JAN 16 WPIDS/WPINDEX/WPIX enhanced with IPC 8 reclassification data
NEWS 6 JAN 22 CA/CAPLUS updated with revised CAS roles
NEWS 7 JAN 22 CA/CAPLUS enhanced with patent applications from India
NEWS 8 JAN 29 PHAR reloaded with new search and display fields
NEWS 9 JAN 29 CAS Registry Number crossover limit increased to 300,000 in
multiple databases
NEWS 10 FEB 15 PATDPASPC enhanced with Drug Approval numbers
NEWS 11 FEB 15 RUSSIAPAT enhanced with pre-1994 records
NEWS 12 FEB 23 KOREAPAT enhanced with IPC 8 features and functionality
NEWS 13 FEB 26 MEDLINE reloaded with enhancements
NEWS 14 FEB 26 EMBASE enhanced with Clinical Trial Number field
NEWS 15 FEB 26 TOXCENTER enhanced with reloaded MEDLINE
NEWS 16 FEB 26 IFICDB/IFIPAT/IFIUDB reloaded with enhancements
NEWS 17 FEB 26 CAS Registry Number crossover limit increased from 10,000
to 300,000 in multiple databases
NEWS 18 MAR 15 WPIDS/WPIX enhanced with new FRAGHITSTR display format
NEWS 19 MAR 16 CASREACT coverage extended
NEWS 20 MAR 20 MARPAT now updated daily
NEWS 21 MAR 22 LWPI reloaded
NEWS 22 MAR 30 RDISCLOSURE reloaded with enhancements
NEWS 23 MAR 30 INPADOCDB will replace INPADOC on STN
NEWS 24 APR 02 JICST-EPLUS removed from database clusters and STN

NEWS EXPRESS NOVEMBER 10 CURRENT WINDOWS VERSION IS V8.01c, CURRENT
MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP),
AND CURRENT DISCOVER FILE IS DATED 25 SEPTEMBER 2006.

NEWS HOURS STN Operating Hours Plus Help Desk Availability
NEWS LOGIN Welcome Banner and News Items
NEWS IPC8 For general information regarding STN implementation of IPC 8

Enter NEWS followed by the item number or name to see news on that
specific topic.

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agreement. Please note that this agreement limits use to scientific
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of commercial gateways or other similar uses is prohibited and may
result in loss of user privileges and other penalties.

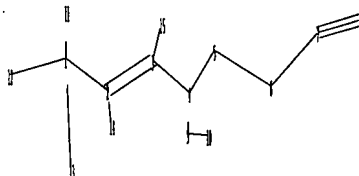
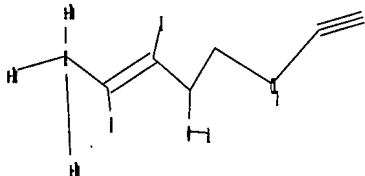
10528256.trn

***** STN Columbus *****

FILE 'HOME' ENTERED AT 12:37:35 ON 19 APR 2007

=>

Uploading C:\Program Files\Stnexp\Queries\10528256.str



chain nodes :

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

chain bonds :

1-2 1-11 1-12 1-13 2-3 2-14 3-4 3-15 4-5 4-9 5-6 6-7 7-8 9-10

exact/norm bonds :

4-9 9-10

exact bonds :

1-2 1-11 1-12 1-13 2-3 2-14 3-4 3-15 4-5 5-6 6-7 7-8

Match level :

1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:CLASS 6:CLASS 7:CLASS 8:CLASS 9:CLASS
10:CLASS 11:CLASS 12:CLASS 13:CLASS 14:CLASS 15:CLASS

ou in the current file, enter

"HELP COMMANDS" at an arrow prompt (=>).

=>

0 IS NOT A RECOGNIZED COMMAND

The previous command name entered was not recognized by the system.

For a list of commands available to you in the current file, enter

"HELP COMMANDS" at an arrow prompt (=>).

=>

0 IS NOT A RECOGNIZED COMMAND

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For a list of commands available to you in the current file, enter

"HELP COMMANDS" at an arrow prompt (=>).

=>

0 IS NOT A RECOGNIZED COMMAND

The previous command name entered was not recognized by the system.

10528256.trn

For a list of commands available to you in the current file, enter "HELP COMMANDS" at an arrow prompt (=>).

=>

0 IS NOT A RECOGNIZED COMMAND

The previous command name entered was not recognized by the system.

For a list of commands available to you in the current file, enter

"HELP COMMANDS" at an arrow prompt (=>).

=>

Uploading

THIS COMMAND NOT AVAILABLE IN THE CURRENT FILE

Do you want to switch to the Registry File?

Choice (Y/n):

Switching to the Registry File...

Some commands only work in certain files. For example, the EXPAND command can only be used to look at the index in a file which has an index. Enter "HELP COMMANDS" at an arrow prompt (=>) for a list of commands which can be used in this file.

=> FILE REGISTRY

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

0.42

0.42

FILE 'REGISTRY' ENTERED AT 12:38:31 ON 19 APR 2007

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STRUCTURE FILE UPDATES: 18 APR 2007 HIGHEST RN 930838-51-0

DICTIONARY FILE UPDATES: 18 APR 2007 HIGHEST RN 930838-51-0

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH December 2, 2006

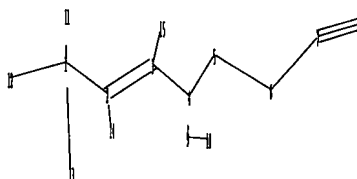
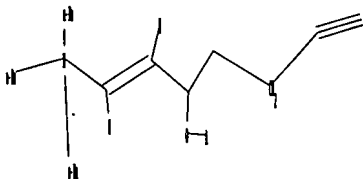
Please note that search-term pricing does apply when conducting SmartSELECT searches.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/ONLINE/UG/regprops.html>

=>

Uploading C:\Program Files\Stnexp\Queries\10528256.str



10528256.trn

chain nodes :

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

chain bonds :

1-2 1-11 1-12 1-13 2-3 2-14 3-4 3-15 4-5 4-9 5-6 6-7 7-8 9-10

exact/norm bonds :

4-9 9-10

exact bonds :

1-2 1-11 1-12 1-13 2-3 2-14 3-4 3-15 4-5 5-6 6-7 7-8

Match level :

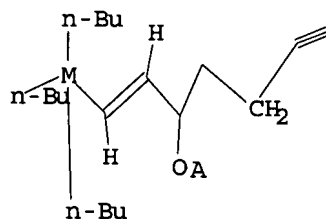
1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:CLASS 6:CLASS 7:CLASS 8:CLASS 9:CLASS
10:CLASS 11:CLASS 12:CLASS 13:CLASS 14:CLASS 15:CLASS

L1 STRUCTURE UPLOADED

=> d l1

L1 HAS NO ANSWERS

L1 STR



Structure attributes must be viewed using STN Express query preparation.

=> s l1

SAMPLE SEARCH INITIATED 12:38:46 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 2568 TO ITERATE

77.9% PROCESSED 2000 ITERATIONS

0 ANSWERS

INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**

BATCH **COMPLETE**

PROJECTED ITERATIONS: 48321 TO 54399

PROJECTED ANSWERS: 0 TO 0

L2 0 SEA SSS SAM L1

=> s l1 sss full

FULL SEARCH INITIATED 12:38:53 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 50300 TO ITERATE

100.0% PROCESSED 50300 ITERATIONS

SEARCH TIME: 00.00.01

L3 3 SEA SSS FUL L1

3 ANSWERS

10528256.trn

=> FIL HCAPLUS

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

172.10

172.52

FILE 'HCAPLUS' ENTERED AT 12:38:58 ON 19 APR 2007

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FILE COVERS 1907 - 19 Apr 2007 VOL 146 ISS 17

FILE LAST UPDATED: 18 Apr 2007 (20070418/ED)

New CAS Information Use Policies, enter HELP USAGETERMS for details.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s l3

L4

~~2 L3~~

=> d l4 ibib abs hitstr tot

L4 ANSWER 1 OF 2 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2005:1250987 HCAPLUS

DOCUMENT NUMBER: 144:150147

TITLE: Fully Stereocontrolled Total Syntheses of the Prostacyclin Analogues 16S-Iloprost and 16S-3-Oxa-Iloprost by a Common Route, Using Alkenylcopper-Azoalkene Conjugate Addition, Asymmetric Olefination, and Allylic Alkylation

AUTHOR(S): Kramp, Guido J.; Kim, Mikhail; Gais, Hans-Joachim; Vermeeren, Cornelia

CORPORATE SOURCE: Institut fuer Organische Chemie, Rheinisch-Westfaelische Technische Hochschule (RWTH) Aachen, Aachen, D-52056, Germany

SOURCE: Journal of the American Chemical Society (2005), 127(50), 17910-17920

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 144:150147

GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB In this article we describe fully stereocontrolled total syntheses of 16S-iloprost (16S-2) I (X = CH₂), the most active component of the drugs Ilomedin and Ventavis, and of 16S-3-oxa-iloprost (16S-3) I (X = O), a close analog of 16S-2 having the potential for a high oral activity, by a new and common route. The key steps of this route are (1) the establishment of the complete C13-C20 ω side chain of the target mols. through a stereoselective conjugate addition of the alkenylcopper derived from enyne II (R = OSiMe₂CMe₃, R₁ = H) to the bicyclic C6-C12 azoalkene III with formation of the corresponding 12-alkylated derivative, (2) the diastereoselective olefination of ketone IV with a chiral phosphoryl acetate, and (3) the regio- and stereoselective alkylation of the allylic acetate V with cuprate Li[Cu(CH₂)₃OSiMe₂CMe₃]₂. These measures allowed the 5E,15S,16S-stereoselective synthesis of 16S-2 and 16S-3, a goal which had previously not been achieved. The configuration at C16 of ω-side chain building block, the alkenylcopper derived from II (R = OSiMe₂CMe₃, R₁ = H), has been installed with high stereoselectivity by the oxazolidinone method and that at C15 by a diastereoselective oxazaborolidine-catalyzed reduction of the C13-C20 ketone II (RR₁ = O) (VI) with catechol borane. Surprisingly, a high diastereoselectivity in the reduction of VI was only obtained by using 2 equiv of oxazaborolidine VII. Application of substoichiometric amts. of VII resulted in irreproducible diastereoselectivities ranging from very high to nil.

IT 873949-42-9P 873949-55-4P

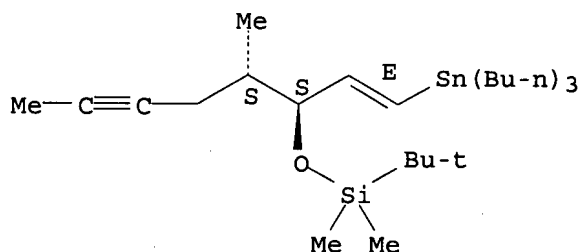
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(asym. synthesis of prostacyclin analogs 16S-iloprost and 16S-3-oxa-iloprost via conjugate addition, olefination, and regio- and stereoselective allylic alkylation)

RN 873949-42-9 HCAPLUS

CN Silane, (1,1-dimethylethyl)dimethyl[[[(1S,2S)-2-methyl-1-[(1E)-2-(tributylstannyl)ethenyl]-4-hexynyl]oxy]- (9CI) (CA INDEX NAME)

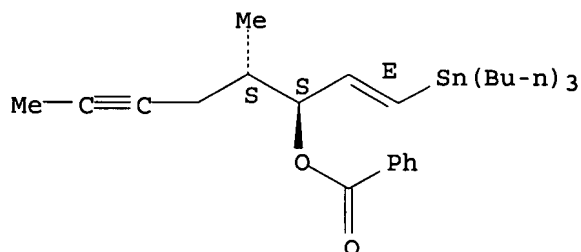
Absolute stereochemistry. Rotation (-).
Double bond geometry as shown.



RN 873949-55-4 HCAPLUS

CN 1-Octen-6-yn-3-ol, 4-methyl-1-(tributylstannyl)-, benzoate, (1E,3S,4S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).
Double bond geometry as shown.



REFERENCE COUNT: 129 THERE ARE 129 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 2 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2004:269993 HCAPLUS

DOCUMENT NUMBER: 140:270668

TITLE: Process for preparing prostaglandin derivatives and starting materials for the same

INVENTOR(S): Kim, Yong Hyun; Lee, Yiu Suk

PATENT ASSIGNEE(S): Yongsung Fine Chemical Co. Ltd., S. Korea

SOURCE: PCT Int. Appl., 20 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

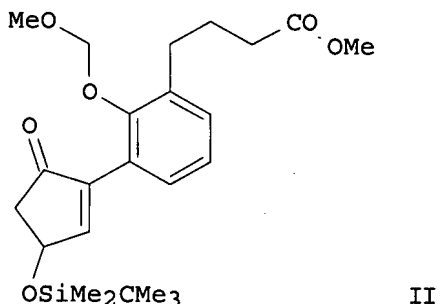
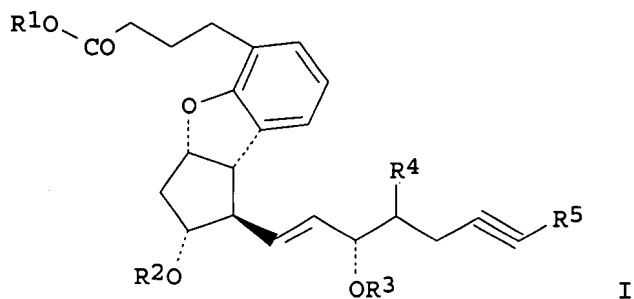
FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004026224	A2	20040401	WO 2003-KR1902	20030918
WO 2004026224	A3	20040624		
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
AU 2003263622	A1	20040408	AU 2003-263622	20030918
CN 1681800	A	20051012	CN 2003-821476	20030918
JP 2005539079	T	20051222	JP 2004-538037	20030918
US 2005272943	A1	20051208	US 2005-528256	20050317
PRIORITY APPLN. INFO.:			KR 2002-56836	A 20020918
			WO 2003-KR1902	W 20030918

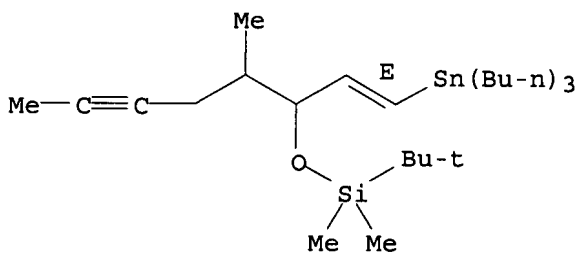
OTHER SOURCE(S): CASREACT 140:270668; MARPAT 140:270668

GI



- AB This present invention provides a process for preparing benzoprostacycline derivs., such as I [R1 = cation, H, alkyl; R2, R3 = H, hydroxyl protecting group; R4, R5 = H, alkyl], i.e. 5,6,7-trinor-4,8-inter-m-phenylene PGI2 derivs., and vinyl tin compds. Bu₃SnCH:CHCH(OR₃)CHR₄CH₂C.tplbond.CR₅ as starting materials for the same. Thus, benzoprostacycline derivative I (R1 = R4 = R5 = Me, R2 = R3 = H) was prepared via a series of steps which included a coupling reaction with 83% yield achieved by using CuCN in THF at 0°, followed by MeLi in Et₂O and adding Bu₃SnCH:CHCH(OSiMe₂CMe₃)CHMeCH₂C.tplbond.CMe at -65° and finally adding a THF solution of ester II at -35°.
- IT 674796-22-6P
 RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (process for preparation of prostaglandin derivs. and starting materials for the same)
- RN 674796-22-6 HCAPLUS
- CN Silane, (1,1-dimethylethyl)dimethyl[[2-methyl-1-[(1E)-2-(tributylstannyl)ethenyl]-4-hexynyl]oxy]- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



10528256.trn

=> FIL REGISTRY

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

20.94

193.46

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE

TOTAL

ENTRY

SESSION

CA SUBSCRIBER PRICE

-1.56

-1.56

FILE 'REGISTRY' ENTERED AT 12:41:35 ON 19 APR 2007

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STRUCTURE FILE UPDATES: 18 APR 2007 HIGHEST RN 930838-51-0

DICTIONARY FILE UPDATES: 18 APR 2007 HIGHEST RN 930838-51-0

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH December 2, 2006

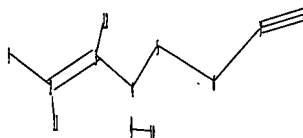
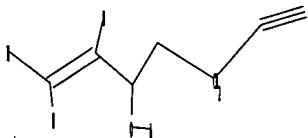
Please note that search-term pricing does apply when conducting SmartSELECT searches.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/ONLINE/UG/regprops.html>

=>

Uploading C:\Program Files\Stnexp\Queries\10528256a.str



chain nodes :

1 2 3 4 5 6 7 8 9 10 11 12

chain bonds :

1-2 2-3 2-11 3-4 3-12 4-5 4-9 5-6 6-7 7-8 9-10

exact/norm bonds :

4-9 9-10

exact bonds :

1-2 2-3 2-11 3-4 3-12 4-5 5-6 6-7 7-8

Match level :

1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:CLASS 6:CLASS 7:CLASS 8:CLASS 9:CLASS
10:CLASS 11:CLASS 12:CLASS

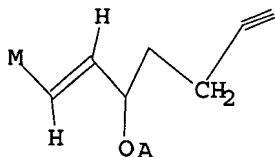
10528256.trn

L5 STRUCTURE UPLOADED

=> d l5

L5 HAS NO ANSWERS

L5 STR



Structure attributes must be viewed using STN Express query preparation.

=> s l5

SAMPLE SEARCH INITIATED 12:41:51 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 4049 TO ITERATE

49.4% PROCESSED 2000 ITERATIONS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01

0 ANSWERS

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**

PROJECTED ITERATIONS: 77164 TO 84796
PROJECTED ANSWERS: 0 TO 0

L6 0 SEA SSS SAM L5

=> s l5 sss full

FULL SEARCH INITIATED 12:41:58 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 80700 TO ITERATE

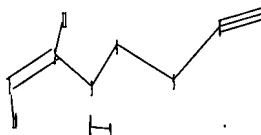
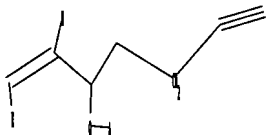
100.0% PROCESSED 80700 ITERATIONS
SEARCH TIME: 00.00.01

3 ANSWERS

L7 3 SEA SSS FUL L5

=>

Uploading C:\Program Files\Stnexp\Queries\10528256b.str



chain nodes :

1 2 3 4 5 6 7 8 9 10 11

chain bonds :

1-10 1-2 2-3 2-11 3-4 3-8 4-5 5-6 6-7 8-9

exact/norm bonds :

3-8 8-9

exact bonds :

1-10 1-2 2-3 2-11 3-4 4-5 5-6 6-7

10528256.trn

Match level :

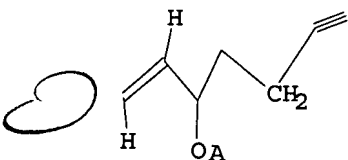
1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:CLASS 6:CLASS 7:CLASS 8:CLASS 9:CLASS
10:CLASS 11:CLASS

L8 STRUCTURE UPLOADED

=> d l8

L8 HAS NO ANSWERS

L8 STR



Structure attributes must be viewed using STN Express query preparation.

=> s l8

SAMPLE SEARCH INITIATED 12:43:21 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 1494 TO ITERATE

100.0% PROCESSED 1494 ITERATIONS

15 ANSWERS

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**

BATCH **COMPLETE**

PROJECTED ITERATIONS: 27562 TO 32198

PROJECTED ANSWERS: 68 TO 532

L9 15 SEA SSS SAM L8

=> s l8 sss full

FULL SEARCH INITIATED 12:43:27 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 30732 TO ITERATE

100.0% PROCESSED 30732 ITERATIONS

SEARCH TIME: 00.00.01

380 ANSWERS

L10 380 SEA SSS FUL L8

=> FIL HCAPLUS

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

344.65

538.11

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE

TOTAL

ENTRY

SESSION

CA SUBSCRIBER PRICE

0.00

-1.56

FILE 'HCAPLUS' ENTERED AT 12:43:31 ON 19 APR 2007

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FILE COVERS 1907 - 19 Apr 2007 VOL 146 ISS 17
FILE LAST UPDATED: 18 Apr 2007 (20070418/ED)

New CAS Information Use Policies, enter HELP USAGETERMS for details.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> d his

(FILE 'HOME' ENTERED AT 12:37:35 ON 19 APR 2007)

FILE 'REGISTRY' ENTERED AT 12:38:31 ON 19 APR 2007

L1 STRUCTURE UPLOADED
L2 0 S L1
L3 3 S L1 SSS FULL

FILE 'HCAPLUS' ENTERED AT 12:38:58 ON 19 APR 2007

L4 2 S L3

FILE 'REGISTRY' ENTERED AT 12:41:35 ON 19 APR 2007

L5 STRUCTURE UPLOADED
L6 0 S L5
L7 3 S L5 SSS FULL
L8 STRUCTURE UPLOADED
L9 15 S L8
L10 380 S L8 SSS FULL

FILE 'HCAPLUS' ENTERED AT 12:43:31 ON 19 APR 2007

=> s 17

L11 2 L7

=> s 110

L12 105 L10

=> s 112 and metal

1729126 METAL
871629 METALS
2098697 METAL

(METAL OR METALS)

L13 7 L12 AND METAL

=> s 112 and Sn

208745 SN
3629 SNS
211544 SN

10528256.trn

(SN OR SNS)

L14 0 L12 AND SN

=> d l11 ibib abs hitstr tot

L11 ANSWER 1 OF 2 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2005:1250987 HCAPLUS

DOCUMENT NUMBER: 144:150147

TITLE: Fully Stereocontrolled Total Syntheses of the Prostacyclin Analogues 16S-Iloprost and 16S-3-Oxa-Iloprost by a Common Route, Using Alkenylcopper-Azoalkene Conjugate Addition, Asymmetric Olefination, and Allylic Alkylation

AUTHOR(S): Kramp, Guido J.; Kim, Mikhail; Gais, Hans-Joachim; Vermeeren, Cornelia

CORPORATE SOURCE: Institut fuer Organische Chemie, Rheinisch-Westfaelische Technische Hochschule (RWTH) Aachen, Aachen, D-52056, Germany

SOURCE: Journal of the American Chemical Society (2005), 127(50), 17910-17920

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 144:150147

GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB In this article we describe fully stereocontrolled total syntheses of 16S-iloprost (16S-2) I (X = CH₂), the most active component of the drugs Ilomedin and Ventavis, and of 16S-3-oxa-iloprost (16S-3) I (X = O), a close analog of 16S-2 having the potential for a high oral activity, by a new and common route. The key steps of this route are (1) the establishment of the complete C13-C20 ω side chain of the target mols. through a stereoselective conjugate addition of the alkenylcopper derived from enyne II (R = OSiMe₂CMe₃, R₁ = H) to the bicyclic C6-C12 azoalkene III with formation of the corresponding 12-alkylated derivative, (2) the diastereoselective olefination of ketone IV with a chiral phosphoryl acetate, and (3) the regio- and stereoselective alkylation of the allylic acetate V with cuprate Li[Cu(CH₂)₃OSiMe₂CMe₃]₂. These measures allowed the 5E,15S,16S-stereoselective synthesis of 16S-2 and 16S-3, a goal which had previously not been achieved. The configuration at C16 of ω -side chain building block, the alkenylcopper derived from II (R = OSiMe₂CMe₃, R₁ = H), has been installed with high stereoselectivity by the oxazolidinone method and that at C15 by a diastereoselective oxazaborolidine-catalyzed reduction of the C13-C20 ketone II (RR₁ = O) (VI) with catechol borane. Surprisingly, a high diastereoselectivity in the reduction of VI was only obtained by using 2 equiv of oxazaborolidine VII. Application of substoichiometric amts. of VII resulted in irreproducible diastereoselectivities ranging from very high to nil.

IT 873949-42-9P 873949-55-4P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

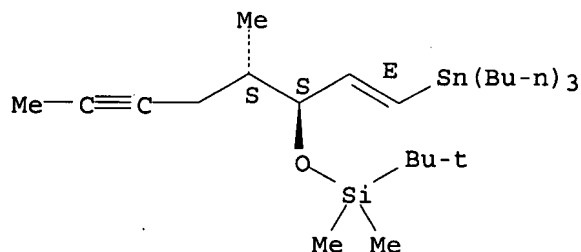
(asym. synthesis of prostacyclin analogs 16S-iloprost and 16S-3-oxa-iloprost via conjugate addition, olefination, and regio- and stereoselective allylic alkylation)

10528256.trn

RN 873949-42-9 HCAPLUS

CN Silane, (1,1-dimethylethyl)dimethyl[[(1S,2S)-2-methyl-1-[(1E)-2-(tributylstannyl)ethenyl]-4-hexynyl]oxy]- (9CI) (CA INDEX NAME)

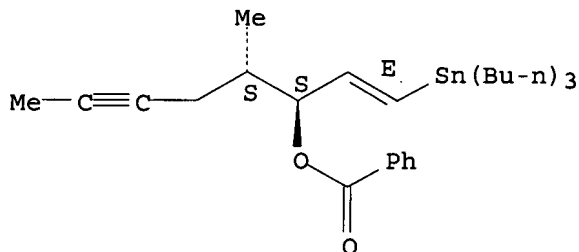
Absolute stereochemistry. Rotation (-).
Double bond geometry as shown.



RN 873949-55-4 HCAPLUS

CN 1-Octen-6-yn-3-ol, 4-methyl-1-(tributylstannyl)-, benzoate, (1E,3S,4S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).
Double bond geometry as shown.



REFERENCE COUNT: 129 THERE ARE 129 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 2 OF 2 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2004:269993 HCAPLUS

DOCUMENT NUMBER: 140:270668

TITLE: Process for preparing prostaglandin derivatives and starting materials for the same

INVENTOR(S): Kim, Yong Hyun, Lee, Yiu Suk

PATENT ASSIGNEE(S): Yonsung Fine Chemical Co. Ltd., S. Korea

SOURCE: PCT Int. Appl., 20 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004026224	A2	20040401	WO 2003-KR1902	20030918
WO 2004026224	A3	20040624		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,				

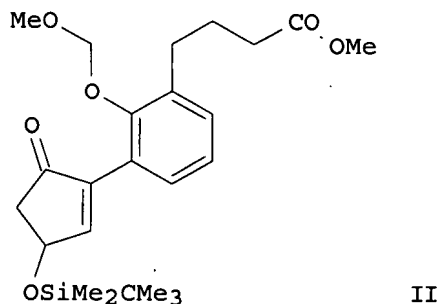
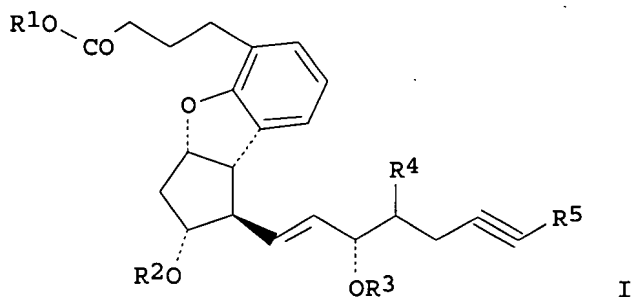
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW

RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

AU 2003263622	A1	20040408	AU 2003-263622	20030918
CN 1681800	A	20051012	CN 2003-821476	20030918
JP 2005539079	T	20051222	JP 2004-538037	20030918
US 2005272943	A1	20051208	US 2005-528256	20050317

PRIORITY APPLN. INFO.: KR 2002-56836 A 20020918
WO 2003-KR1902 W 20030918

OTHER SOURCE(S): CASREACT 140:270668; MARPAT 140:270668
GI



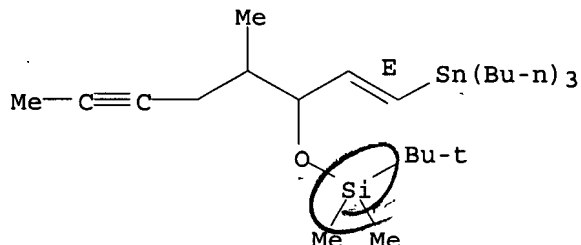
- AB This present invention provides a process for preparing benzoprostacycline derivs., such as I [R1 = cation, H, alkyl; R2, R3 = H, hydroxyl protecting group; R4, R5 = H, alkyl], i.e. 5,6,7-trinor-4,8-inter-m-phenylene PGI2 derivs., and vinyl tin compds. Bu3SnCH:CHCH(OR3)CHR4CH2C.tplbond.CR5 as starting materials for the same. Thus, benzoprostacycline derivative I (R1 = R4 = R5 = Me, R2 = R3 = H) was prepared via a series of steps which included a coupling reaction with 83% yield achieved by using CuCN in THF at 0°, followed by MeLi in Et2O and adding Bu3SnCH:CHCH(OSiMe2CMe3)CHMeCH2C.tplbond.CMe at -65° and finally adding a THF solution of ester II at -35°.
- IT 674796-22-6P
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(process for preparation of prostaglandin derivs. and starting materials for the same)

10528256.trn

RN 674796-22-6 HCAPLUS

CN Silane, (1,1-dimethylethyl)dimethyl[[2-methyl-1-[(1E)-2-(tributylstannyl)ethenyl]-4-hexynyl]oxy]-(9CI) (CA INDEX NAME)

Double bond geometry as shown.



=> d l13 ibib abs hitstr tot

L13 ANSWER 1 OF 7 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2005:1287338 HCAPLUS

DOCUMENT NUMBER: 144:170933

TITLE: Enantioselective palladium-catalyzed addition of 1,3-dicarbonyl compounds to an allene derivative

AUTHOR(S): Trost, Barry M.; Simas, Alessandro B. C.; Plietker, Bernd; Jakel, Christoph; Xie, Jia

CORPORATE SOURCE: Department of Chemistry, Stanford University, Stanford, CA, 94305-5080, USA

SOURCE: Chemistry--A European Journal (2005), 11(23), 7075-7082

CODEN: CEUJED; ISSN: 0947-6539

PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 144:170933

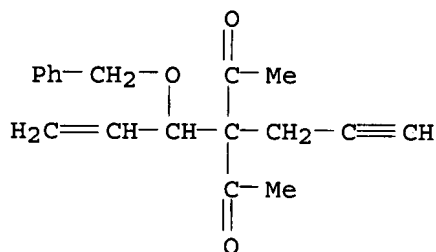
AB Enhancing atom economy of the metal-catalyzed asym. allylic alkylation (AAA) shifts from the usual nucleophilic displacement of a leaving group to an addition of a pronucleophile to a double bond. Using 1-alkoxyallenes as proelectrophiles, the palladium-catalyzed AAA proceeds with 1,3-dicarbonyl compds. as pronucleophiles with excellent regioselectivity and enantiomeric excess under optimized conditions. The pH of the medium proved crucial for reactivity/selectivity. By using the more acidic Meldrum's acids, the reactions required a co-catalytic amount of Bronsted acid, such as trifluoroacetic acid. Single regioisomeric products of 82-99% ee were obtained. On the other hand, the less acidic 1,3-diketones failed to react under such conditions. The fact that a less acidic acid like benzoic acid sufficed, suggested the need for general base catalysis as well. Thus, a mixture of triethylamine and benzoic acid proved optimal (ee's 93-99). Employment of the (R,R)-Ph Trost ligand gave a product with S configuration. A model to rationalize the results has been developed.

IT 874484-05-6P

RL: SPN (Synthetic preparation); PREP (Preparation)
(enantioselective palladium-catalyzed addition of 1,3-dicarbonyl compds. to an allene derivative)

RN 874484-05-6 HCAPLUS

CN 2,4-Pentanedione, 3-[1-(phenylmethoxy)-2-propenyl]-3-(2-propynyl)-(9CI)
(CA INDEX NAME)



REFERENCE COUNT: 47 THERE ARE 47 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L13 ANSWER 2 OF 7 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1996:554974 HCAPLUS

DOCUMENT NUMBER: 125:300496

TITLE: Titanocene-Catalyzed Cyclocarbonylation of Enynes to Cyclopentenones

AUTHOR(S): Hicks, Frederick A.; Kablaoui, Natasha M.; Buchwald, Stephen L.

CORPORATE SOURCE: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA

SOURCE: Journal of the American Chemical Society (1996), 118(39), 9450-9451

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 125:300496

AB The conversion of enynes to cyclopentenones catalyzed by $\text{Cp}_2\text{Ti}(\text{CO})_2$ is described. This system produces cyclopentenones in excellent yields (75-95%) and displays functional group tolerance unprecedented in Group 4 metallocene chemical. Substrates containing 1,2-disubstituted olefins are also cleanly cyclized, leading to the first transition metal -catalyzed cyclocarbonylative route to tricyclic cyclopentenones.

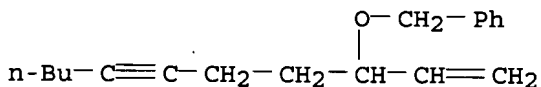
IT 158044-33-8

RL: RCT (Reactant); RACT (Reactant or reagent)

(titanocene-catalyzed cyclocarbonylation of enynes to cyclopentenones)

RN 158044-33-8 HCAPLUS

CN Benzene, [[(1-ethenyl-4-nonyl)oxy]methyl]- (9CI) (CA INDEX NAME)



L13 ANSWER 3 OF 7 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1994:700492 HCAPLUS

DOCUMENT NUMBER: 121:300492

TITLE: Pd-Catalyzed Cycloisomerization to 1,2-Dialkylidenecycloalkanes. 1

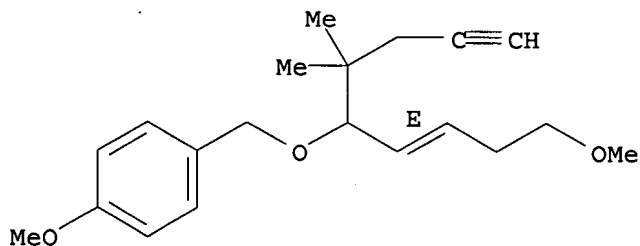
AUTHOR(S): Trost, Barry M.; Tanoury, Gerald J.; Lautens, Mark; Chan, Chuen; MacPherson, David T.

CORPORATE SOURCE: Department of Chemistry, Stanford University, Stanford, CA, 94035-5080, USA

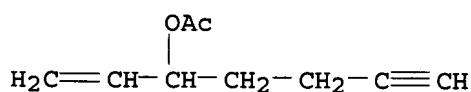
SOURCE: Journal of the American Chemical Society (1994),
 116(10), 4255-67
 CODEN: JACSAT; ISSN: 0002-7863
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 121:300492

- AB Enhancing synthetic efficiency requires the development of synthetic reactions that, to the extent possible, are simple addns. wherein everything else is required only in catalytic amts. The Alder ene reaction constitutes a classical reaction that meets this requirement that has much unrealized potential. A transition-metal-catalyzed version helps to increase that potential by permitting this reaction to proceed under mild conditions. A significant benefit of transition metal catalysis is the feasibility of diverting the reaction along pathways not feasible under thermal conditions. The synthesis of 1,3-dienes rather than 1,4-dienes is a very important diversion because of the utility of 1,3-dienes as reaction partners in the Diels-Alder reaction, another highly atom economical process. A catalyst derived from palladium acetate cycloisomerizes 1,6- and 1,7-enynes to dialkylidenecyclopentanes and -cyclohexanes. 1,3-Diene formation is favored over the Alder ene process by both steric and electronic effects. The reaction is highly chemoselective - tolerating a wide diversity of functionality including hydroxyl groups, ketones, esters, alkynyl and enol ethers, alkynyl and vinyl silanes, and enones. Many of the substrates are available by palladium-catalyzed alkylation reactions - highlighting the effectiveness of palladium catalyzed methodol. in organic synthesis. The atom-economical nature of these reactions combined with the Diels-Alder reaction permit butadiene and di-Me propargylmalonate to be molded into a polyhydro-as-indacene. The mechanism of this reaction may involve a tautomerization of an enyne-Pd(+2) complex to a pallada(+4)cyclopentene intermediate as a key step.
- IT 131152-54-0
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (Alder ene reaction of)
- RN 131152-54-0 HCAPLUS
- CN Benzene, 1-methoxy-4-[[[1-(4-methoxy-1-butenyl)-2,2-dimethyl-4-pentynyl]oxy]methyl]-, (E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



- IT 159009-85-5
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (palladium-catalyzed allylic alkylation of)
- RN 159009-85-5 HCAPLUS
- CN 1-Hepten-6-yn-3-ol, acetate (9CI) (CA INDEX NAME)



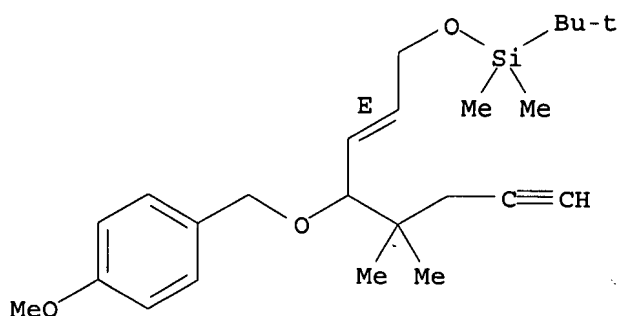
IT 159009-65-1

RL: RCT (Reactant); RACT (Reactant or reagent)
(palladium-catalyzed stereoselective cycloisomerization of)

RN 159009-65-1 HCAPLUS

CN Silane, (1,1-dimethylethyl)[[4-[(4-methoxyphenyl)methoxy]-5,5-dimethyl-2-octen-7-ynyl]oxy]dimethyl-, (E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



L13 ANSWER 4 OF 7 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1994:605159 HCAPLUS

DOCUMENT NUMBER: 121:205159

TITLE: Development of a Titanocene-Catalyzed Enyne
Cyclization/Isocyanide Insertion Reaction

AUTHOR(S): Berk, Scott C.; Grossman, Robert B.; Buchwald, Stephen
L.

CORPORATE SOURCE: Department of Chemistry, Massachusetts Institute of
Technology, Cambridge, MA, 02139, USA

SOURCE: Journal of the American Chemical Society (1994),
116(19), 8593-601

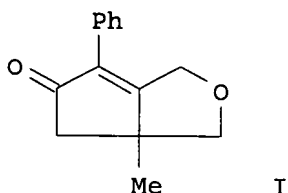
CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 121:205159

GI



AB The first early transition-metal-catalyzed enyne cyclization
reaction is described. The system converts enyne substrates, e.g.,
PhC.tplbond.CCH2OCH2CMe:CH2, to bicyclic iminocyclopentenones through the

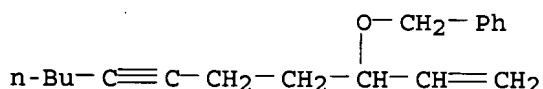
use of 10 mol % of $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ in the presence of a silyl cyanide. Subsequent hydrolysis produces the corresponding bicyclic cyclopentenones, e.g., I, in good overall yield. The cyclization reaction is tolerant of polar functional groups such as ethers, amines, and esters and is diastereoselective with certain chiral enyne substrates.

IT 158044-33-8P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(stereoselective titanocene-catalyzed enyne cyclization-isocyanide insertion reaction)

RN 158044-33-8 HCAPLUS

CN Benzene, [[(1-ethenyl-4-nonyl)oxy]methyl]- (9CI) (CA INDEX NAME)



L13 ANSWER 5 OF 7 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1993:212536 HCAPLUS

DOCUMENT NUMBER: 118:212536

TITLE: A $[\text{W}(\text{CO})_5\cdot\text{THF}]$ -mediated Pauson-Khand reaction: cyclizations of 1,6-enynes via a batch-catalytic protocol

AUTHOR(S): Hoye, Thomas R.; Suriano, Joseph A.

CORPORATE SOURCE: Dep. Chem., Univ. Minnesota, Minneapolis, MN, 55455, USA

SOURCE: Journal of the American Chemical Society (1993), 115(3), 1154-6

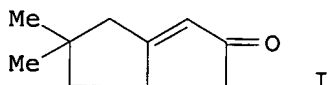
CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 118:212536

GI



AB Tungsten pentacarbonyl·THF has been shown to mediate Pauson-Khand-like cyclizations of a series of 1,6-enynes to generate bicyclo[3.3.0]oct-1-en-3-ones (e.g., I from $\text{HC.tplbond.CCH}_2\text{CMe}_2\text{CH}_2\text{CH:CH}_2$). Cobalt and iron carbonyls are the only metal carbonyls known to effect this transformation. Substrates containing either electron deficient alkenes or electron deficient alkynes participate in the tungsten-promoted reaction. Similarities and differences with the customary $\text{Co}_2(\text{CO})_8$ -induced cyclization are discussed. A major advantage is the fact that tungsten hexacarbonyl, the sole source of metal atoms, can be recovered very efficiently upon exposing the reaction mixture to an atmospheric of carbon monoxide after consumption of the enyne.

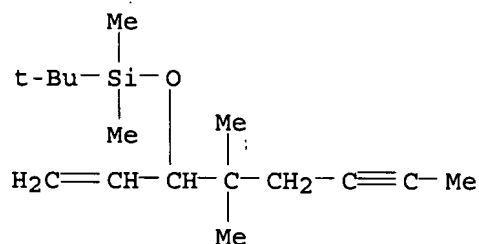
IT 146917-54-6

RL: RCT (Reactant); RACT (Reactant or reagent)

(Pauson-Khand cyclization of, with tungsten pentacarbonyl)

RN 146917-54-6 HCAPLUS

CN Silane, (1,1-dimethylethyl) [(1-ethenyl-2,2-dimethyl-4-hexynyl)oxy]dimethyl-
(9CI) (CA INDEX NAME)



L13 ANSWER 6 OF 7 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1991:142706 HCAPLUS

DOCUMENT NUMBER: 114:142706

TITLE: Annulation via alkylation-Alder ene cyclizations.

Palladium-catalyzed cycloisomerization of 1,6-enynes

AUTHOR(S): Trost, Barry M.; Lautens, M.; Chan, C.; Jebaratnam, D. J.; Mueller, T.

CORPORATE SOURCE: Dep. Chem., Univ. Wisconsin, Madison, WI, 53706, USA

SOURCE: Journal of the American Chemical Society (1991),
113(2), 636-44

CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 114:142706

AB Pd(0) catalyzed alkylation of an allyl substrate with a nucleophile containing a double or triple bond to permit subsequent thermal Alder ene reactions constitutes a novel annulation protocol. In the case of a triple bond, a Pd(2+) complex catalyzes 1 equivalent of an Alder ene reaction. This new cyclization is probed in terms of the effect of substitution of the olefin, the acetylene, and the tether connecting the two. The reaction produces both 1,4-dienes (Alder ene-type products) and 1,3-dienes. Mechanisms to account for the diversity of products are presented. The Pd(2+)-catalyzed reaction shows an ability to interact with remote nonreactive parts of substrate to affect conformation and thereby selectivity. Several advantages accrue to the Pd(2+)-catalyzed reaction. First, the reaction normally proceeds at 25-65° instead of the >250° (in static systems) to >500° (in flow systems) for the thermal reaction. Second, reactions that fail thermally succeed via the metal-catalyzed process. Third, complementary regioselectivity may be observed. Fourth, the ligating properties of the metal catalyst offer opportunities for exercising control not possible in a simple thermal process. A novel cyclopentannulation of allyl alc. and related derivs. evolves in which Pd(0) catalyzes formation of the 1st bond and a simple electronic switch to Pd(2+) catalyzes formation of the 2nd bond.

IT 131130-45-5P 131130-47-7P 131152-54-0P

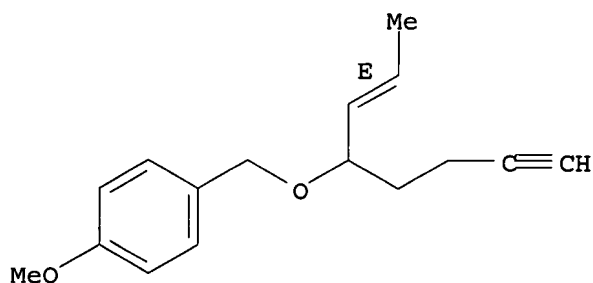
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and intramol. cycloaddn. reaction of)

RN 131130-45-5 HCAPLUS

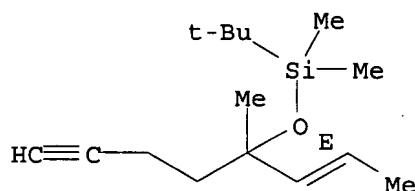
CN Benzene, 1-methoxy-4-[[[1-(1-propenyl)-4-pentynyl]oxy]methyl]-, (E)- (9CI)
(CA INDEX NAME)

Double bond geometry as shown.



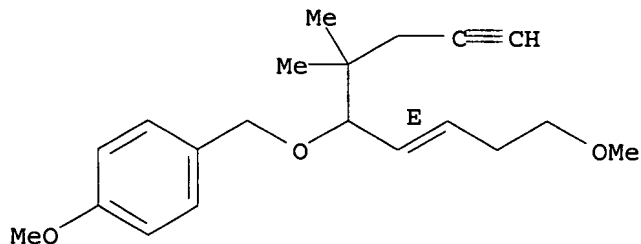
RN 131130-47-7 HCAPLUS
 CN Silane, (1,1-dimethylethyl)dimethyl[[1-methyl-1-(1-propenyl)-4-pentynyl]oxy]-, (E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



RN 131152-54-0 HCAPLUS
 CN Benzene, 1-methoxy-4-[[[1-(4-methoxy-1-butenyl)-2,2-dimethyl-4-pentynyl]oxy]methyl]-, (E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



L13 ANSWER 7 OF 7 HCAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 1986:552237 HCAPLUS
 DOCUMENT NUMBER: 105:152237
 TITLE: Reduction of compounds containing carbon-carbon triple bonds
 INVENTOR(S): Shibasaki, Masakatsu; Sodeoka, Mikiko; Ogawa, Yuji
 PATENT ASSIGNEE(S): Sagami Chemical Research Center, Japan
 SOURCE: Jpn. Kokai Tokkyo Koho, 8 pp.
 CODEN: JKXXAF
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 61078735	A	19860422	JP 1984-198721	19840925
JP 05040734	B	19930621		

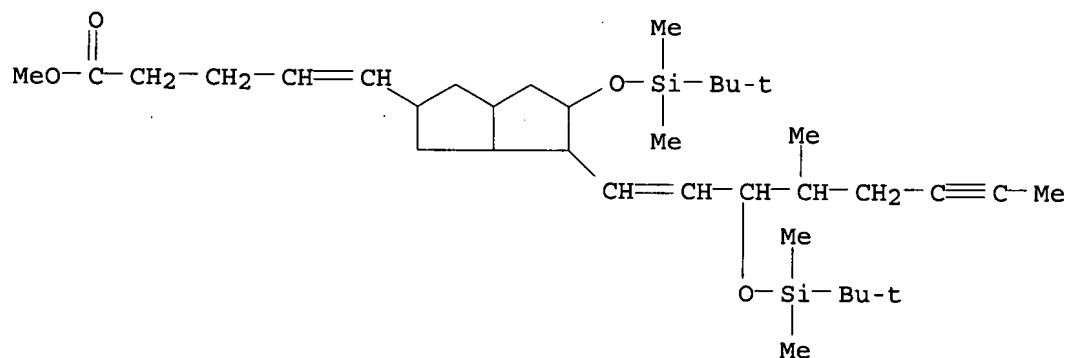
PRIORITY APPLN. INFO.: JP 1984-198721 19840925
 OTHER SOURCE(S): CASREACT 105:152237

AB Isolated carbon-carbon triple bonds in organic compds. are selectively reduced with H to cis double bonds in the presence of $\text{MR}(\text{CO})_3$ (M = metal in VIB group; R = polycyclic organic compound). Thus, heating 100 mg 1-Ph-1-propyne, 45 mg tricarbonylnaphthalenechromium, and 100 mg n-pentadecane (internal standard) in 2 mL THF under H (20 kg/cm²) at 45° for 24 h gave 92% cis- β -methylstyrene.

IT 104602-92-8
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reduction of, in presence of organometallic carbonyl complex)

RN 104602-92-8 HCAPLUS

CN 4-Pentenoic acid, 5-[5-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-4-[3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-4-methyl-1-octen-6-ynyl]octahydro-2-pentalenyl]-, methyl ester (9CI) (CA INDEX NAME)



=> log y

COST IN U.S. DOLLARS

FULL ESTIMATED COST

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

CA SUBSCRIBER PRICE

SINCE FILE

ENTRY

55.23

SINCE FILE

ENTRY

-7.02

TOTAL

SESSION

593.34

TOTAL

SESSION

-8.58

STN INTERNATIONAL LOGOFF AT 12:45:10 ON 19 APR 2007